

# Molecular Structure and Binding Energies of Monosubstituted Hexacarbonyls of Chromium, Molybdenum, and Tungsten: Relativistic Density Functional Study

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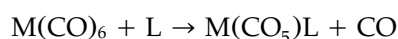
**ABSTRACT:** Relativistic density functional calculations have been carried out for the group VI transition metal carbonyls  $M(\text{CO})_5\text{L}$  ( $M = \text{Cr, Mo, W}$ ;  $\text{L} = \text{OH}_2, \text{NH}_3, \text{PH}_3, \text{PMe}_3, \text{N}_2, \text{CO, OC (isocarbonyl), CS, CH}_2, \text{CF}_2, \text{CCl}_2, \text{NO}^+$ ). The optimized molecular structures and  $\text{M—L}$  bond dissociation energies, as well as the metal–carbonyl bond energy of the trans CO group, have been calculated. Besides the marked dependence of the trans  $\text{M—CO}$  bond length on the type of ligand  $\text{L}$ , such an effect on the that bond energy is also observed. For the chromium compounds, the trans  $\text{Cr—CO}$  bond length varies from 184 to 199 pm and its bond energy from 242 to 150 kJ/mol. For the molybdenum compounds, the range is 197 to 216 pm and 253 to 128 kJ/mol and, for tungsten, 198 to 214 pm and 293 to 159 kJ/mol. The observed trends can be explained with the  $\pi$  acceptor strength of the  $\text{L}$  ligand. © 1997 John Wiley & Sons, Inc. *J Comput Chem* **18**: 1985–1992, 1997

**Keywords:** density functional; relativistic; calculation; transition metal; carbonyl; trans effect

## Introduction

The hexacarbonyls of chromium, molybdenum, and tungsten may be regarded as prototypes of low-valent donor–acceptor complexes formed by these metals. For the oxidation state 0,

the 18-electron rule requires (for monodentate ligands) a sixfold coordination of the central metal atom, which then usually has an octahedral environment. In the same way as the hexacarbonyls can be viewed as prototypes of a large class of transition metal compounds, the substitution reaction:



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might be considered as an important model for chemical reactions involving such molecules. Therefore, the molecular structure and the stability of the monosubstituted hexacarbonyls deserve some attention. Moreover, these data depend sensitively on the type of ligand L and can thus give information on the properties of the ligand.

The structure and the first metal–carbonyl bond dissociation energy of the hexacarbonyls of chromium, molybdenum, and tungsten are well known from experimentation. However, few such data are available for the monosubstituted hexacarbonyls of this study. In the case of the pentacarbonyl thiocarbonyls, bond dissociation energies obtained by mass spectroscopy are available,<sup>1</sup> whereas the attempts to determine molecular structure by X-ray diffraction have failed due to structural disorder (between the CO and CS groups) in the solid state.<sup>2</sup> In the case of  $\text{Cr}(\text{CO})_5\text{PH}_3$ , a complete X-ray analysis was also prevented by the same problem.<sup>3</sup> For the trimethylphosphines, experimental structural data are available.<sup>4–6</sup> Some of the dinitrogen complexes covered in the present work have been studied in low-temperature matrices.<sup>7,8</sup> Combining UV photolysis and vibrational spectroscopy, it was possible to elucidate general patterns of the molecular structure, but no information on bond lengths could be obtained this way. For a related compound, the dinitrogen binding energy could be estimated<sup>9</sup> through the kinetics of the decay of the matrix-isolated species.

In recent years, quantum chemical calculations for transition metal compounds have reached a level of accuracy that enables them to provide useful data. It is possible to determine molecular structure and binding energies in cases where experimental numbers are difficult (or even practically impossible) to get. Moreover, the results of an *a priori* calculation of the structure and stability of yet unknown compounds is valuable information only theory can provide.

A critical evaluation of the results of Kohn–Sham density functional calculations shows that this method is generally able to yield accurate molecular structures, and to predict binding energies at least semiquantitatively. The necessary prerequisites are the use of a gradient-corrected (“nonlocal”) exchange–correlation functional and the consideration of relativistic effects, which become increasingly important if 4d or 5d transition metal atoms are present in the complex. For reviews see refs. 10 and 11.

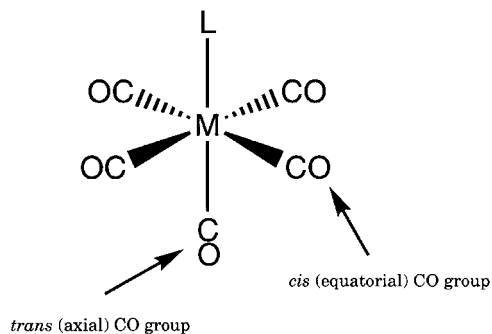


FIGURE 1. Cis and trans CO ligands in  $\text{M}(\text{CO})_5\text{L}$ .

In this study, results from Kohn–Sham density functional calculations (with relativistic corrections as proposed recently<sup>12</sup>) are presented for a series of monosubstituted hexacarbonyls of the group VI metals Cr, Mo, and W. The results include the molecular structures of compounds  $\text{M}(\text{CO})_5\text{L}$  for various ligands L, namely for  $\text{OH}_2$ ,  $\text{NH}_3$ ,  $\text{PH}_3$ ,  $\text{PMe}_3$ ,  $\text{N}_2$ , CO, OC (isocarbonyl), CS,  $\text{CH}_2$ ,  $\text{CF}_2$ ,  $\text{CCl}_2$ , and  $\text{NO}^+$ , as well as for unsaturated 16-electron pentacarbonyls. The M–L binding energy is evaluated as well as the binding energy of the trans (axial) metal–carbonyl bond (see Fig. 1), the latter depending strongly on the type of the ligand L.

Some of these data, namely the M–L bond length and the M–L bond energy for the diatomic ligands  $\text{N}_2$ , CO, CS, and  $\text{NO}^+$ , have been published elsewhere<sup>13</sup> and have been compared with calculations performed by other investigators or, where possible, with experimental results. These comparisons have established that the performance of the present method is satisfactory. In this work, such additional comparisons will be made for the phosphine complexes, which have been well studied experimentally, and for the methylene complexes, for which some recent computational results can be found in the literature.

## Computational Method

The calculations have been performed with the present investigator's implementation of a Kohn–Sham density functional program,<sup>14</sup> in which first-order relativistic corrections (by direct perturbation theory) have been built in.<sup>12</sup> Computational details can be found in ref. 13. Briefly, DZP basis sets have been used for the ligand atoms, while the transition metal atoms carry fairly large basis sets. As compared to ref. 13, the basis

sets for molybdenum and tungsten have been augmented by an additional set of  $p$  functions, taking the next exponent of the well-tempered series. This affected the results only marginally. The gradient-corrected ("nonlocal") density functional of Becke<sup>15</sup> and Perdew<sup>16</sup> has been used in all calculations. An important feature of the program is its high numerical accuracy because the electrostatic Coulomb energy is evaluated analytically and high-quality grids have been used for the numerical integration of the exchange-correlation energy.

The binding energies have been corrected for the basis set superposition effect (BSSE). The major contribution to the BSSE is the energy lowering of the dissociating ligand due to the basis functions located at the larger fragment. The BSSE correction is important as it can affect the bond dissociation energy by as much as 30 kJ/mol in the case of the  $\text{CF}_2$  ligand, which is an extreme case in this respect; typical values of the BSSE correction are about 15 kJ/mol for ligand basis sets used in this study. Differences in zero-point vibrational energy and thermal corrections to the binding energy tend to cancel each other<sup>17</sup> and have not been evaluated.

The hexacarbonyls have been optimized within  $O_h$  symmetry. A  $C_{4v}$  symmetry has been assumed for the pentacarbonyls and the  $\text{M}(\text{CO})_5\text{L}$  complexes with diatomic ligands. For the unsaturated

pentacarbonyls, one might also consider a  $D_{3h}$  (trigonal bipyramidal) structure and, for the dinuclear complexes, side-on coordination might be competitive. In these two cases, however, a  $C_{4v}$  structure has been deduced experimentally<sup>7,18</sup> through the analysis of the vibrational spectra of the matrix-isolated compounds.  $C_s$  symmetry restrictions have been imposed for the optimization of the structure of the phosphine and ammonia complexes, and staggered  $C_{2v}$  structures (implying equivalent equatorial [cis] carbonyl ligands) have been assumed for the carbene complexes ( $\text{L} = \text{CH}_2, \text{CF}_2, \text{CCl}_2$ ) and the water complex. For all molecules studied, the angles between the metal–ligand bonds were close to those found in a regular octahedron. In the case of  $\text{Cr}(\text{CO})_5\text{CH}_2$ , the effect of a rotation of the methylene group has been looked at by performing a calculation for the eclipsed  $C_{2v}$  structure as well (see Table I). There is almost no effect on the (average) equatorial metal–carbonyl bond lengths. The other bond lengths change slightly, and binding energies are hardly affected by methylene rotation.

## Results and Discussion

Tables I to III contain the results of the calculations on chromium, the molybdenum, and tung-

**TABLE I.**  
Results for Chromium Complexes  $\text{Cr}(\text{CO})_5\text{L}$ .

L	$R(\text{Cr—L})$ [pm]	$R(\text{Cr—C}_{\text{ax}})$ [pm]	$R(\text{Cr—C}_{\text{eq}})$ [pm]	$D_e(\text{Cr—L})$ [kJ/mol]	$D_e(\text{Cr—CO}_{\text{ax}})$ [kJ/mol]
$\diamond$	—	183.0	190.3	—	—
$\text{OH}_2$	218.5	184.4	189.9	70	242
OC	214.0	184.9	190.5	30	230
$\text{NH}_3$	220.0	185.5	189.6	121	233
$\text{PH}_3$	235.9	186.9	189.5	129	213
$\text{PMe}_3$	239.1	187.0	188.9	164	214
$\text{N}_2$	196.1	187.7	190.7	94	205
CO	190.5	190.5	190.5	183	183
$\text{CF}_2^{\text{a}}$	193.7	191.1	190.3	211	177
$\text{CCl}_2^{\text{a}}$	194.2	192.0	190.7	223	166
CS	186.9	193.0	190.7	249	167
$\text{CH}_2^{\text{a}}$	191.4	193.5	190.6	344 <sup>b</sup>	164
$\text{CH}_2^{\text{c}}$	192.1	193.1	190.7	341 <sup>b</sup>	166
$\text{NO}^+$	174.9	199.4	194.8	431	150

<sup>a</sup> Staggered  $C_{2v}$  conformation.

<sup>b</sup> This bond energy refers to the dissociation of singlet methylene. The singlet–triplet splitting of methylene calculated by the present method, 72 kJ/mol, has to be subtracted to yield the energy of the dissociation of triplet methylene.

<sup>c</sup> Eclipsed  $C_{2v}$  conformation.

TABLE II.  
Results for Molybdenum Complexes Mo(CO)<sub>5</sub>L.

L	<i>R</i> (Mo—L) [pm]	<i>R</i> (Mo—C <sub>ax</sub> ) [pm]	<i>R</i> (Mo—C <sub>eq</sub> ) [pm]	<i>D<sub>e</sub></i> (Mo—L) [kJ / mol]	<i>D<sub>e</sub></i> (Mo—CO <sub>ax</sub> ) [kJ / mol]
◇	—	194.5	205.7	—	—
OH <sub>2</sub>	234.6	197.3	205.5	62	253
OC	231.1	197.4	205.9	27	242
NH <sub>3</sub>	236.0	199.3	205.3	108	231
PH <sub>3</sub>	252.7	201.7	205.5	116	199
PMe <sub>3</sub>	254.9	202.2	205.1	153	194
N <sub>2</sub>	212.8	201.7	206.2	83	202
CO	206.4	206.4	206.4	163	163
CF <sub>2</sub> <sup>a</sup>	209.1	207.5	206.3	191	153
CCl <sub>2</sub> <sup>a</sup>	209.0	208.4	206.7	205	142
CS	202.4	209.5	206.8	228	142
CH <sub>2</sub> <sup>a</sup>	205.0	211.7	206.8	321 <sup>b</sup>	128
NO <sup>+</sup>	188.8	215.7	210.2	426	140

<sup>a</sup> Staggered C<sub>2v</sub> conformation.  
<sup>b</sup> Dissociation to singlet methylene (see footnote b in Table I).

sten compounds. The first line in each table (L = ◇) reports the molecular structure of the unsaturated pentacarbonyl. Whereas the equatorial metal-carbon bond length of the three pentacarbonyls is similar to the metal-carbon bond length in the corresponding hexacarbonyl (see L = CO in Tables I–III), the trans (axial) bond length is substantially shorter, by 7 to 10 pm. This effect has previously been documented from MP2 (second-order Moller–Plesset) calculations.<sup>17</sup> As an aside, the ne-

glect of the geometry relaxation of the pentacarbonyl fragment was the source of a systematic error in bond energy calculations from the last decade,<sup>19</sup> when full geometry optimizations at a relativistic level of theory, which are routine now,<sup>12,20</sup> were not yet possible.  
Now, if one looks at the molecular structure of the monosubstituted hexacarbonyls, one finds the same pattern: Whereas the equatorial cis metal-carbonyl bond length is hardly affected

TABLE III.  
Results for Tungsten Complexes W(CO)<sub>5</sub>L.

L	<i>R</i> (W—L) [pm]	<i>R</i> (W—C <sub>ax</sub> ) [pm]	<i>R</i> (W—C <sub>eq</sub> ) [pm]	<i>D<sub>e</sub></i> (W—L) [kJ / mol]	<i>D<sub>e</sub></i> (W—CO <sub>ax</sub> ) [kJ / mol]
◇	—	194.6	205.2	—	—
OH <sub>2</sub>	231.6	197.5	205.0	80	293
OC	225.5	198.0	205.4	37	278
NH <sub>3</sub>	233.5	199.4	204.8	132	269
PH <sub>3</sub>	251.8	201.5	205.1	138	233
PMe <sub>3</sub>	254.2	202.0	204.8	182	227
N <sub>2</sub>	209.9	202.2	205.9	107	233
CO	206.1	206.1	206.1	193	193
CF <sub>2</sub> <sup>a</sup>	209.3	206.6	205.9	224	184
CCl <sub>2</sub> <sup>a</sup>	209.1	207.4	206.2	239	173
CS	202.5	208.5	206.3	264	173
CH <sub>2</sub> <sup>a</sup>	205.4	210.0	206.3	362 <sup>b</sup>	159
NO <sup>+</sup>	188.7	214.4	209.3	456	165

<sup>a</sup> Staggered C<sub>2v</sub> conformation.  
<sup>b</sup> Dissociation to singlet methylene (see footnote b in Table I).

upon substitution (with the exception of  $L = \text{NO}^+$ ), the axial (trans) bond length depends strongly on the substituting ligand  $L$ . The axial bond length varies from 184 to 199 pm for the chromium compounds, from 197 to 216 pm for molybdenum, and from 198 to 214 pm for tungsten. Ehlers and coworkers<sup>21</sup> have also found a similar effect in their MP2 calculations, and they established a correlation between the axial metal–carbonyl bond length and the amount of  $\pi$ -backbonding toward the ligand  $L$ , which they evaluated using charge decomposition analysis (CDA). This “trans effect”<sup>22</sup> had actually been well known<sup>23,24</sup>; a good  $\pi$  acceptor reduces the amount of backbonding to the other ligands, and this effect is stronger on the trans ligand because a pair of trans ligands share two metal  $d$  orbitals of appropriate symmetry, whereas only one such orbital is shared by a pair of cis ligands. A significant effect of the substituting ligand  $L$  on the cis metal–carbonyl bond length can only be observed in the case of the nitrosyl cation ligand. This may not only be attributed to the  $\pi$  acidity of this ligand, but also to the fact that it is positively charged.

It should be noted that this effect manifests itself in the  $\text{C}=\text{O}$  bond lengths as well: A reduction of backbonding to the trans carbonyl ligand strengthens (and shortens) its  $\text{C}=\text{O}$  bond. In the present calculations, the axial  $\text{C}=\text{O}$  bond length for the pentacarbonyl phosphines, pentacarbonyl isocarbonyls, and unsaturated pentacarbonyls was 0.5 to 1 pm longer than in the corresponding hexacarbonyl, whereas this bond length was 1.5 pm shorter in the case of the nitrosyl cation complexes, where it was even slightly shorter than in free carbon monoxide. Furthermore, the trans effect has an impact on the interaction of the  $\text{C}=\text{O}$  stretching modes in metal carbonyls because stretching a CO ligand makes it a better  $\pi$  acceptor. These rules have already been formulated in Kraihanzel and Cotton’s classical study<sup>25</sup> on the analysis of vibrational spectra of metal carbonyls. For the same reason, the  $A_{1g}$   $\text{C}=\text{O}$  stretching mode of the hexacarbonyls, where all  $\text{C}=\text{O}$  bonds stretch simultaneously, has the highest frequency.<sup>26</sup>

The isocarbonyl complexes in Tables I to III are somewhat hypothetical, but this ligand has been included because pentacarbonyl isocarbonyl species have been discussed—but experimentally excluded—as a possible product after photolysis of the corresponding hexacarbonyl in a low-temperature matrix.<sup>18,27</sup> The present calculations predict that the isocarbonyl binding energy is much lower than for the dinitrogen ligand. Because very low

temperature matrices (at  $\sim 20$  K) were required to observe the dinitrogen complexes,<sup>7</sup> the computational result is consistent with the fact that no isocarbonyl species could be observed. The metal–ligand bond energy for water, which has the lowest  $\pi$  acidity of all ligands studied here, is also predicted to be lower than for the dinitrogen ligand.

In addition to the trans effect on bond lengths, there is also such an effect on the trans metal–carbonyl bond energies. This problem has only been addressed rarely from the theoretical perspective.<sup>24,28</sup> The binding energies in the last columns of Tables I to III have been obtained after a complete geometry optimization of the  $\text{M}(\text{CO})_4\text{L}$  fragments (with the four carbonyls in the basal positions of a square pyramid) and corrected for the BSSE. Note that all entries within these columns refer to a metal–carbonyl binding energy, so the variation is quite large: chromium–carbonyl binding energies range from 242 down to 150 kJ/mol, and the range is 253 to 128 kJ/mol for the molybdenum and 293 to 159 kJ/mol for the tungsten compounds. The trend in the axial metal–carbonyl binding energy is not unexpected and follows the trend for the the bond length: ligands  $L$ , which are strong  $\pi$  acceptors, tend to decrease the backbonding to the trans carbonyl ligand. Therefore, the trans metal–carbonyl bond length increases and its bond energy decreases. For weak  $\pi$  acceptors, the situation is reversed. For molybdenum and tungsten, to remove the trans CO group is more difficult for  $\text{M}(\text{CO})_5\text{NO}^+$  than for  $\text{M}(\text{CO})_5\text{CH}_2$ , although the trans metal–carbon bond length is much longer for the nitrosyl complexes. This might be caused by  $\text{NO}^+$  being a charged ligand, leading to an extra destabilization of the unsaturated fragment  $\text{M}(\text{CO})_4\text{NO}^+$ .

Many experimental data are available for pentacarbonyl phosphine complexes. Table IV contains a compilation of the present results together with experimental data for pentacarbonyl phosphines (where available) and pentacarbonyl trimethyl phosphines. A complete set of data is available for the trimethyl phosphines, whereas, in the case of (parent) phosphines, an X-ray structure is available only for the chromium compound,<sup>3</sup> and even this one suffers from structural disorder. The metal–phosphorus bond lengths obtained in this work are longer than for the unsubstituted phosphines and are too long, by 2 to 4 pm, compared with the experimental values. If the calculation is repeated with two sets of polarization functions on the phosphorus atoms (e.g., with expo-

**TABLE IV.**  
**Present Results and Experimental Data for Phosphine Complexes.**

Compound	$R(\text{M}-\text{PR}_3)$ [pm]	$R(\text{M}-\text{C}_{\text{ax}})$ [pm]	$R(\text{M}-\text{C}_{\text{eq}})$ [pm]	Source
$\text{Cr}(\text{CO})_5\text{PH}_3$	235.9	186.9	189.5	This work
	235.0			Ref. 3
$\text{Cr}(\text{CO})_5\text{PMe}_3$	239.1	187.0	188.9	This work
	236.6	185.0	189.3	Ref. 4
$\text{Mo}(\text{CO})_5\text{PH}_3$	252.7	201.7	205.5	This work
$\text{Mo}(\text{CO})_5\text{PMe}_3$	254.9	202.2	205.1	This work
	250.8	198.4	203.6	Ref. 5
$\text{W}(\text{CO})_5\text{PH}_3$	251.8	201.5	205.1	This work
$\text{W}(\text{CO})_5\text{PMe}_3$	254.2	202.0	204.8	This work
	251.6	200.0	201.0	Ref. 6

nents such as those used by Pacchioni and Bagus<sup>28</sup>), the metal-phosphorus bond distance shrinks by only 0.5 pm. The trans metal-carbonyl bond lengths are also shorter than those found experimentally. However, the latter are sometimes difficult to obtain experimentally. Note that the experimental structure for  $\text{W}(\text{CO})_5\text{PMe}_3$ <sup>6</sup> reports a rather small difference between the axial and (average) equatorial tungsten-carbonyl bond length, which does not match the pattern observed for the other compounds. The investigators suggested that the experimental uncertainties might be larger than the differences in the W—C bond lengths. This seems to be the case indeed, because problems in the experimental structure determination are indicated by the large differences between the individual equatorial W—C bond lengths (with range from 198 to 203 pm) and between the equatorial C—O bond lengths (from 113 to 119 pm). According to the calculations, these differences should be much smaller. The calculated trans metal-carbonyl bond lengths indicate that the  $\pi$  acidity of trimethylphosphine is not so much larger than the  $\pi$  acidity of the unsubstituted phosphine ligand. It may be conjectured that the bond energy of the metal-trimethylphosphine bond is higher because it is a better  $\sigma$  donor. The P—R bond distances in the  $\text{PR}_3$  ligand are shorter in the complex than in the free ligand [ $\text{PH}_3$ : 144.1 pm,  $\text{M}(\text{CO})_5\text{PH}_3$ : 143.3 pm;  $\text{PMe}_3$ : 187.0 pm,  $\text{M}(\text{CO})_5\text{PMe}_3$ : 185.0 pm]. If a phosphine ligand approaches the metal center from an infinite distance, the P—R bond length begins to shrink already at a large metal-phosphorus distance. This is probably the consequence of changing an (*s*-type) lone pair into a metal-phosphorus bond. The overall shortening of the P—R bond therefore gives

little insight into the amount of backbonding. On the other hand, a small variation of the metal-phosphorus bond length around its equilibrium value induces an opposite variation of the P—R bond length. This is consistent with assuming backbonding into the P—R  $\sigma^*$  orbitals of the ligand. A detailed investigation of the electronic properties of phosphine ligands is beyond the scope of this study and will be given elsewhere.<sup>29</sup>

Let us now have a closer look at the results for the carbene complexes. In Table V, the metal-carbene bond lengths, the axial metal-carbonyl bond lengths, and the metal-methylene binding energies obtained in the present work and from other calculations can be found. Density functional results for  $\text{Cr}(\text{CO})_5\text{CF}_2$  and  $\text{Cr}(\text{CO})_5\text{CCl}_2$  were recently published,<sup>30</sup> but only at the LDA level and are thus of no use for comparison with the present data. For the fluorocarbenes, MP2 data from Ehlers and coworkers<sup>21</sup> are available, but the binding energy could not be obtained at the coupled cluster level at that time due to program limitations; however, an MP2 estimate using isostructural reactions is available.

The amount of backbonding to the methylene ( $\text{CH}_2$ ) ligand in the calculation of Ehlers and coworkers<sup>21</sup> was rather low for the chromium complex (i.e., lower than in chromium hexacarbonyl). This result is unexpected, but somehow consistent with their finding that the axial Cr—CO bond length in  $\text{Cr}(\text{CO})_5\text{CH}_2$  should be *shorter* than in chromium hexacarbonyl. However, intuition suggests that methylene is a stronger  $\pi$  acceptor than carbonyl in these complexes and that the axial Cr—CO bond length in  $\text{Cr}(\text{CO})_5\text{CH}_2$  should then be *longer* than in chromium hexacarbonyl, as is found in the present work and in the results of Ziegler

**TABLE V.**  
**Selected Computational Results for Carbene Complexes.**

Compound	$R(\text{M}-\text{CR}_2)$ [pm]	$R(\text{M}-\text{C}_{\text{ax}})$ [pm]	$D_e(\text{M}-\text{CR}_2)$ [kJ/mol]	Source
$\text{Cr}(\text{CO})_5\text{CH}_2$	191.4	193.5	344	This work
	193.0	195.4	351	QR-DFT <sup>a</sup>
	189.0	185.4	353	CCSD(T) // MP2 <sup>b</sup>
$\text{Cr}(\text{CO})_5\text{CF}_2$	193.7	191.1	211	This work
	190.4	185.6	180	MP2 <sup>c</sup>
$\text{Cr}(\text{CO})_5\text{CCl}_2$	194.2	192.0	223	This work
$\text{Mo}(\text{CO})_5\text{CH}_2$	205.0	211.7	321	This work
	206.1	213.6	335	QR-DFT <sup>a</sup>
	202.8	219.6	353	CCSD(T) // MP2 <sup>b</sup>
$\text{Mo}(\text{CO})_5\text{CF}_2$	209.1	207.5	191	This work
	207.4	212.8	162	MP2 <sup>c</sup>
$\text{Mo}(\text{CO})_5\text{CCl}_2$	209.0	208.4	228	This work
$\text{W}(\text{CO})_5\text{CH}_2$	205.4	210.0	362	This work
	203.4	210.7	380	QR-DFT <sup>a</sup>
	203.1	211.9	380	CCSD(T) // MP2 <sup>b</sup>
$\text{W}(\text{CO})_5\text{CF}_2$	209.3	206.6	224	This work
	205.7	208.3	199	MP2 <sup>c</sup>
$\text{W}(\text{CO})_5\text{CCl}_2$	209.1	207.4	239	This work

<sup>a</sup> “Quasi-relativistic” density functional calculations, refs. 31 and 32. The methylene singlet–triplet splitting calculated in that work, 66 kJ/mol, has been added to the published value, which refers to a dissociation into the pentacarbonyl and triplet methylene.

<sup>b</sup> MP2 geometries (using quasi-relativistic core potentials for Mo and W) and binding energies by the coupled cluster CCSD(T) method (from ref. 21).

<sup>c</sup> MP2 geometries (using quasi-relativistic core potentials for Mo and W) and MP2 binding energies estimated from isostructural reactions (from ref. 21).

et al.<sup>31,32</sup> (their value for chromium hexacarbonyl is 191.0 pm<sup>20</sup>). The metal–ligand bond lengths of the MP2 structures of first-row transition metal compounds are notoriously too short,<sup>21</sup> but in this case there is little doubt that the MP2 calculations fail to reproduce correctly the trend in the bond length.

For the molybdenum and tungsten methylene complexes, all calculations agree that the trans metal–carbonyl bond length should be longer than in the corresponding hexacarbonyl. Compared with the results of the present work and to the quasi-relativistic density functional results of ref. 32, the elongation of the trans metal–carbonyl bond in  $\text{Mo}(\text{CO})_5\text{CH}_2$  is probably overestimated in the MP2 calculations. The same seems to be the case for  $\text{Mo}(\text{CO})_5\text{CF}_2$  and has also been observed for the nitrosyl complex  $\text{Mo}(\text{CO})_5\text{NO}^+$ .<sup>13</sup>

All calculations predict similar bond dissociation energies for the methylene complexes. The values obtained in the present work are consistently lower than in the other calculations. This may be attributed to the BSSE correction, which

has not been considered in other work. The BSSE correction leads to a reduction in binding energies by 15 to 20 kJ/mol for the methylene binding energies, but is probably somewhat smaller if better *ligand* basis sets are used.<sup>33</sup> For all three metals, the metal– $\text{CF}_2$  bond dissociation energy obtained in this work is  $\sim 30$  kJ/mol higher than the MP2 result of Ehlers et al.<sup>21</sup> Because of this discrepancy, it is suggested that these investigators soon evaluate these energies at the CCSD(T) level.

What is the effect if one replaces methylene with the halomethylenes  $\text{CF}_2$  or  $\text{CCl}_2$ ? Because of the interaction of the halogen lone pairs with the empty *p*-orbital at the carbene center, the latter becomes less available for accepting  $\pi$ -backbonding. The availability of the empty *p* orbital can be monitored in the isolated (singlet) carbene by looking at the NMR chemical shift of the carbon atom.<sup>34</sup> The absolute magnetic shieldings of the carbon atom, as calculated with the multiconfiguration IGLO (MC-IGLO) method,<sup>34</sup> is  $-718$  ppm for (singlet)  $\text{CH}_2$ ,  $-101$  ppm for  $\text{CF}_2$ , and  $-346$  ppm

for  $\text{CCl}_2$ . Therefore, the  $\pi$ -acceptor strength should be  $\text{CF}_2 < \text{CCl}_2 < \text{CH}_2$ , and the same ordering is found for the trans metal–carbonyl bond length (and the metal–carbene bond energy) for all three metals. These trends may be helpful for the interpretation of results for experimentally known carbene complexes, where the carbene center is always stabilized with respect to methylene, usually by a heteroatom in the  $\alpha$  position.

## Conclusion

Structural and energetic data for monosubstituted hexacarbonyls of group VI metals have been obtained for a variety of ligands. This data show a correlation with electronic properties ( $\pi$  acidity) of the ligands. Using this correlation, the data obtained in this work can be used to assess the  $\pi$  acidity of other ligands, based on observable quantities such as bond lengths and bond dissociation energies. Work along these lines is in progress.<sup>29</sup>

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